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(21) International Application Number: PCT/EP98/03702 (22) International Filing Date: 11 June 1998 (11.06.98) (30) Priority Data: 97201776.8 12 June 1997 (12.06.97) EP (34) Countries for which the regional or international application was filed: GB et al. (71) Applicant (for all designated States except CA): SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (71) Applicant (for CA only): SHELL CANADA LIMITED [CA/CA]; 400 - 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). (72) Inventors: SCHERMER, Wilhelmina, Elisabeth, Maria; Badhuisweg 3, NL-1031 CM Amsterdam (NL). STEERNBERG, Koen; Badhuisweg 3, NL-1031 CM Amsterdam (NL).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PAVING (57) Abstract The present invention relates to a paving comprising a bitumen composition containing an acid blown bitumen and a polymer containing epoxy groups, which paving is a paving which is in frequent contact with oil fractions, more specifically airfield pavement, buslanes and/or flooring of gas stations; to a process for preparing such bitumen composition, to a composition comprising aggregate and such bitumen composition and to use of such bitumen composition for paving which is in frequent contact with oil fractions.		

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PAVING

The present invention relates to a paving comprising a bitumen composition, to a process for preparing a bitumen composition, to a composition comprising aggregate and bitumen composition and to use
5 of a bitumen composition for airfield pavements, buslanes and/or flooring of gas stations.

Bitumen is used as a binder in road asphalt mixtures. Bitumen compositions commonly used dissolve on prolonged exposure to oil fractions, which softens
10 the pavement surface and can lead to accelerated loss of aggregate. This phenomenon is observed more markedly where the bitumen is more frequently in contact with oil fractions, such as airfield pavements, buslanes and flooring of gas stations. Therefore, it was
15 investigated how the oil resistance, of bitumen compositions could be improved.

Surprisingly, it has now been found that a bitumen composition containing an acid blown bitumen and a polymer containing epoxy groups, has improved resistance
20 to dissolving in oil fractions, i.e. a reduced amount of bitumen dissolves when the sample is immersed in the oil fraction.

The present invention relates to a paving comprising a bitumen composition containing an acid
25 blown bitumen and a polymer containing epoxy groups, which paving is a paving which is in frequent contact with oil fractions. More specifically, the paving is airfield pavement, buslanes and/or flooring of gas stations. Further, the present invention relates to the

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use of such bitumen composition for paving which is in frequent contact with oil fractions.

In WO 96/28513 it is described that a bitumen composition having an improved effective temperature range is obtained by reacting a polymer containing available epoxy groups with a bitumen in the presence of acid. In Example E, it is taught that it is undesirable to use bitumen pretreated with acid. The bitumen compositions obtained are described to be suitable for use in paving in general.

In US-A-5,519,073 it is described that it is advantageous to mix a terpolymer derived from the concurrent reaction of ethylene, normal butyl acrylate and glycidyl ester with an acid blown bitumen if subsequently between 0.2 to 2.0 weight percent of amine anti-stripping additive is added. The compositions are for use in road construction in general.

The acid blown bitumen to be used in the present invention, preferably is a bitumen obtainable by contacting bitumen with oxygen at a temperature of between 240 and 340 °C in the presence of an acid capable of reacting with the bitumen.

All types of bitumen, both naturally occurring and synthetically manufactured, can be used for subjecting to blowing in the presence of an acid. According to the invention, the term "bitumen" is meant to include materials designated by the term "asphalt". No distinction is made between these terms. Naturally occurring bitumen includes bitumens such as native rock asphalt and lake asphalt. Synthetically manufactured bitumen is often a by-product of petroleum refining operations and includes air-blown bitumen, blended bitumen, cracked or residual bitumen, petroleum bitumen,

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propane bitumen, straight run bitumen and thermal bitumen.

The bitumen composition of the present invention comprises acid blown bitumen optionally in combination with other hydrocarbon fractions, such as straight run bitumen. Residual oil fractions, gas oil and/or one or more fluxes can be added to decrease the viscosity. These can be added either to the acid blown bitumen or to the bitumen composition containing the polymer containing epoxy groups. Preferably, they are added to the acid blown bitumen. The bitumen composition preferably comprises 30-100 % by weight of acid blown bitumen, more preferably between 40 and 100 %, based on total amount of hydrocarbon fractions in the bitumen composition.

The acid blown bitumen preferably is a bitumen obtainable by contacting bitumen with oxygen at a temperature of between 240 and 340 °C in the presence of an acid capable of reacting with the bitumen.

The bitumen to be contacted with oxygen in the presence of acid, preferably has a penetration of from 50 to 500 dmm measured by ASTM D5 at 25°C, preferably of from 150 to 250 dmm.

The acid with which the bitumen is to be contacted can be any acid capable of reacting with the bitumen at the temperature mentioned, or precursors of such acids. These precursors form acids capable of reacting with the bitumen, at the reaction conditions. Preferred compounds to be used are one or more compounds chosen from the group of orthophosphoric acid, metaphosphoric acid, phosphonic acid, phosphorous acid, phosphorous pentoxide, phosphinic acid, phosphinous acid, pyrophosphoric acid, polyphosphoric acid, pyrophosphonic

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acid, trimethaphosphoric acid, sulphuric acid, boric acid, boronic acid, one or more alkyl substituents containing derivatives of these acids in which the alkyl substituent contains 1 to 15 carbon atoms, and
5 precursors of these acids. Most preferably, the acid is orthophosphoric acid, metaphosphoric acid, polyphosphoric acid and/or phosphorous pentoxide.

Methods of preparing suitable acid blown bitumen comprising different kinds of bitumen, have been
10 described in EP-A-459 811. In UK patent application 9802312.0, a process has been described by which an acid blown bitumen can be prepared which can be used per se in the present invention.

A preferred acid blown bitumen has a penetration
15 index of at least 0. Measurement of the penetration index has been described in the "The Shell bitumen industrial handbook", ISBN-0-95 16625-1-1, 1995, pages 100-104.

The acid blown bitumen can contain further
20 additives known to be suitable to the skilled person. If an emulsion is to be obtained, water and emulsifier can be present.

The acid blown bitumen preferably has a penetration
of from 15 to 70 as measured by ASTM D5 at 25°C, more
25 preferably from 15 to 40, more specifically 15 to 30.

The polymer containing epoxy groups preferably is a polymer as described in WO-A-96/28513. Further, a curable blend containing the polymer containing epoxy groups in combination with an organic thermosetting
30 resin can be used, as also described in WO-A-96/28513. Other preferred polymers have been described in US-A-5,306,750.

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Preferably, the polymer containing epoxy groups is a polymer comprising:

- (i) 40-90% by weight of ethene, based on polymer,
 - (ii) 0-40% by weight, based on polymer, of a monomer
5 selected from unsaturated mono- and dicarboxylic acids of 3-20 carbon atoms, esters of such acids, vinyl esters of saturated carboxylic acids where the acid group has 1 to 18 carbon atoms, acrylonitrile, methacrylonitrile, alpha-olefins of
10 3-20 carbon atoms, norbornene and vinyl aromatic compounds, and
 - (iii) 0.1-15% weight percent, based on polymer, of an ethylenically unsaturated monomer of 4-21 carbon atoms containing an epoxy group.
- 15 Preferably, the polymer is a terpolymer of ethene, acrylate and glycidylacrylate.

Preferably, the polymer containing epoxy groups is mixed with a solvent before being contacted with the acid blown bitumen. Preferred solvents are water,
20 residual oil fractions, gas oil fractions and fluxes. Most preferably, the polymer containing epoxy groups is mixed with flux, more specifically gas oil flux.

The bitumen composition preferably is a bitumen composition obtainable by contacting the acid blown
25 bitumen with the polymer containing epoxy groups at a temperature of between 120 and 195°C, preferably at a temperature of between 140 and 180°C. The reaction will usually be carried out at ambient pressure.

Preferably, the bitumen composition comprises
30 between 95 and 99.9% by weight of acid blown bitumen and between 0.1 and 5% by weight of polymer containing epoxy groups, weight based on total amount of acid blown bitumen and polymer containing epoxy groups. More

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preferably, the bitumen composition comprises between 95 and 99.8% by weight of acid blown bitumen between 0.2 and 5% by weight of polymer containing epoxy groups.

5 The paving will generally further contain aggregate.

The present invention further relates to a composition comprising aggregate and a bitumen composition containing between 95 and 99.9 % by weight of acid blown bitumen and between 0.1 and 5 % by weight
10 of polymer containing epoxy groups, based on total composition, which composition contains less than 0.2 % by weight of amine anti-stripping additive, based on total composition.

Furthermore, the invention relates to a process for
15 preparing a bitumen composition containing between 95 and 99.9 % by weight of acid blown bitumen and between 0.1 and 5 % by weight of polymer containing epoxy groups, based on total composition, which composition contains less than 0.2% by weight of amine anti-
20 stripping additive, based on total composition, which process comprises contacting bitumen with oxygen at a temperature of between 240 and 340°C in the presence of an acid capable of reacting with the bitumen and subsequently contacting the acid blown bitumen at a
25 temperature of between 120 and 195°C with a polymer containing epoxy groups.

The paving of the present invention will generally contain aggregate, and optionally further conventional additives. If aggregate is present, the paving a of the
30 present invention preferably comprises from 90 to 99% by weight of aggregate and from 1 to 10% by weight of bitumen composition, based on total amount of aggregate and bitumen composition.

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EXAMPLES

An acid blown bitumen was prepared by adding 1.8 %w of phosphoric acid to a bitumen having a penetration of 200 dmm and blowing the mixture at a temperature of 275°C to obtain an acid blown bitumen having a penetration of 60/30 and a penetration index of 4. The acid blown bitumen was mixed with a flux, with straight run bitumen and with heavy gas oil. The base bitumen obtained contained 54 % by weight of acid blown bitumen and had a penetration of 200 pen and a penetration index of + 0.8.

The base bitumen was mixed with polymer using high shear disintegration at a temperature of 180 °C.

The polymers used were the following.

A copolymer of ethene and butylacrylate having a butylacrylate content of 35 %w.

A terpolymer of 28 %w of butylacrylate, 5 %w of glycidylacrylate and the remainder being ethene.

A terpolymer of 24 % methylacrylate, 8 % glycidylmethacrylate and the remainder being ethene.

A specimen of base bitumen and polymer was prepared in accordance with the Marshall method RAW 57. The specimen was immersed in a glass beaker which was filled with enough kerosene to fully submerge the asphalt specimen. After a period of 24 hours the specimen is taken out of the kerosene and dried in a fumeboard with ventilation until the weight does not change anymore. The difference in weight of the asphalt sample before and after exposure is taken as a measure for kerosene resistance.

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	Weight loss (%w)
polymer (% by weight)	
none	6.6
copolymer of ethene and butylacrylate (1%)	6.6
terpolymer of butylacrylate, glycidylacrylate and ethene (1%)	1.3
terpolymer of methylacrylate, glycidylmethacrylate and ethene (1%)	0.8

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C L A I M S

1. Paving comprising a bitumen composition containing an acid blown bitumen and a polymer containing epoxy groups, which paving is a paving which is in frequent contact with oil fractions.
- 5 2. Paving according to claim 1, in which the paving is airfield pavement, buslanes and/or flooring of gas stations.
3. Paving according to claim 1 or 2, in which the acid blown bitumen has a penetration index of at least 0.
- 10 4. Paving according to any one of claims 1-3, in which the acid blown bitumen is obtainable by contacting bitumen with oxygen at a temperature of between 240 and 340 °C in the presence of an acid capable of reacting with the bitumen.
- 15 5. Paving according to any one of claims 1-4, in which the bitumen composition is obtainable by contacting the acid blown bitumen at a temperature of between 120 and 195 °C with a polymer containing epoxy groups.
- 20 6. Paving according to any one of claims 1-5, in which the polymer containing epoxy groups is a polymer comprising:
 - (i) 40-90 % by weight of ethene, based on polymer,
 - (ii) 0-40 % by weight, based on polymer, of a monomer selected from unsaturated mono- and dicarboxylic acids
- 25 of 3-20 carbon atoms, esters of such acids, vinyl esters of saturated carboxylic acids where the acid groups has 1 to 18 carbon atoms, acrylonitrile, methacrylonitrile, alpha-olefins of 3-20 carbon atoms, norbornene and vinyl aromatic compounds, and

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(iii) 0.1-15 % by weight, based on polymer, of an ethylenically unsaturated monomer of 4-21 carbon atoms containing an epoxy group.

5 7. Paving according to any one of claims 1-6, in which the acid blown bitumen has a penetration of from 15 to 70 dmm as measured by ASTM D5 at 25 °C.

8. Paving according to any one of claims 1-7, which paving comprises from 90 to 99 % by weight of aggregate and from 1 to 10 % by weight of bitumen composition,
10 based on total amount of aggregate and bitumen composition.

9. Composition comprising aggregate and a bitumen composition containing between 95 and 99.9 % by weight of acid blown bitumen and between 0.1 and 5 % by weight
15 of polymer containing epoxy groups, based on total composition, which composition contains less than 0.2 % by weight of amine anti-stripping additive, based on total composition.

10. Process for preparing a bitumen composition
20 containing between 95 and 99.9 % by weight of acid blown bitumen and between 0.1 and 5 % by weight of polymer containing epoxy groups, based on total composition, which composition contains less than 0.2 % by weight of amine anti-stripping additive, based on total
25 composition, which process comprises contacting bitumen with oxygen at a temperature of between 240 and 340°C in the presence of an acid capable of reacting with the bitumen and subsequently contacting the acid blown bitumen at a temperature of between 120 and 195°C with a
30 polymer containing epoxy groups.

11. Use of a bitumen composition containing an acid blown bitumen and a polymer containing epoxy groups for paving which is in frequent contact with oil fractions.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/03702

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L95/00 //(C08L95/00,23:08)

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 91 09907 A (CHEVRON RES & TECH) 11 July 1991 see page 5, line 16 - page 10, line 14 see page 16, line 19 - page 18, line 6 & US 5 306 750 A (GOODRICH) cited in the application ---	1-11
Y	WO 96 20250 A (OWENS CORNING FIBERGLASS CORP) 4 July 1996 see page 2, line 14 - page 5, line 2 ---	1-11
Y	US 4 882 373 A (MORAN LYLE E) 21 November 1989 see claims 1-5 --- -/-	1-4



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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